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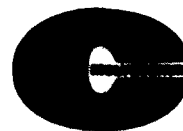
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Detroit, Michigan

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**RESEARCH AND DEVELOPMENT ON NEW PROCESSES
OF PRODUCING DUCTILE MOLYBDENUM**

31 August 1962

Prepared under Navy, Bureau of Naval Weapons

Contract No. NOrd-15915

**Progress Report Covering Period
1 November 1961 - 31 July 1962**

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Detroit, Michigan**

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ABSTRACT

An investigation was carried out for the purpose of determining the practical limits of solid-state purification of unalloyed molybdenum. It was found that by using low-pressure, flowing atmospheres of tank oxygen for decarburization and palladium-diffused hydrogen for deoxidation, the following effects were produced: (a) the carbon content was reduced to 0.003% from 0.019% by weight, (b) minor phases were eliminated from the microstructure, as judged by observations at X2000, (c) the room-temperature hardness was lowered to 158.5 DPH from 168.1 DPH (30 kg load), and (d) the 120°-bend transition temperature was raised slightly, from 365 F up to 390 F.

The specimen temperature had to be limited to about 3250 F to avoid contamination from titanium which was an impurity in the molybdenum susceptor. Consequently, it was not possible to take full advantage of the decarburization reaction which is promoted by high temperatures; therefore, the maximum degree of solid-state decarburization probably was not achieved.

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INTRODUCTION

This report summarizes the research conducted between May 1961 and 31 July 1962. It was one phase of a research program sponsored by the Naval Bureau of Weapons under Contract No. NOrd-15915 on new processes for producing ductile molybdenum. The objective of this phase of the research was to ascertain the practical limits of solid-state purification reactions in unalloyed molybdenum as judged by hardness and bend ductility measurements. This report completes this phase of the research program being conducted under Contract No. NOrd-15915.

The basis for the investigation was twofold: (a) thermodynamic data indicated that purification of solid molybdenum with respect to the common interstitial impurities ought to occur at high temperatures in a vacuum and/or in special gaseous atmospheres, and (b) experimental results in other laboratories, e.g., the Battelle Memorial Institute (1)*, had shown that solid-state purification reactions in vacuo can occur at a rate fast enough to produce measurable results in a reasonable time. Unfortunately, in many instances of reported research on solid-state purification of molybdenum, the ultimate degree of purification was either (a) limited by the design of the purification apparatus, or (b) unknown because of problems of chemical analysis. The two most common limitations imposed by experimental apparatuses were the inability to attain vacua better than 0.1 or 0.01 μ (10^{-4} - 10^{-5} mm) Hg and contamination by carbon from vapors from oil diffusion pumps and/or vacuum waxes and greases.

The present investigation was undertaken on the assumption that the apparatus design problem could be solved by the use of an all-glass, high-vacuum system employing a high-capacity, three-stage, mercury diffusion pump in conjunction with two cold traps. In this system the possibility of contamination from mechanical pump oil vapor would be essentially nonexistent since the vapor would have to back-diffuse through the powerful mercury pump and through two liquid nitrogen cold traps to reach the purification chamber. Also, the minute amount of mercury vapor that might back-diffuse past the two cold traps would be inconsequential in view of the passivity of molybdenum toward mercury. The need for vacuum grease or wax would be eliminated by the all-glass construction of the vacuum system. Access to the purification chamber would be gained by glass-blowing techniques on each run. A detailed description of the apparatus constructed and used under the present contract is presented later in the report.

It was assumed that with the type of apparatus described above, interstitial impurity levels in molybdenum could be lowered to the point where current analytical techniques would not be capable of giving reliable analyses. Therefore, it was planned to monitor the degree of purification by hardness and bend ductility determinations as described later in the EXPERIMENTAL PROCEDURES section.

* Numbers in parentheses pertain to references listed at the end of the text.

THEORY OF SOLID-STATE PURIFICATION

Stated simply, solid-state purification consists of the diffusion of impurities to the surface of a solid where they escape by volatilization or by reaction to form a gaseous compound. The most common mode of solid-state refining is vacuum annealing at high temperatures. This will remove hydrogen, nitrogen, and oxygen from unalloyed molybdenum by the volatilization of these elements as gases, preceded by the thermal dissociation of any oxides and nitrides which may be present. Carbon can be removed by reaction with oxygen or hydrogen to form CO or hydrocarbon gases, respectively. In the temperature range where solid-state refining of molybdenum is usually carried out, however, hydrocarbon gases are thermally unstable, and decarburization by this mechanism probably is minor. Wet hydrogen has been used successfully (2) at high temperatures, probably because CO rather than hydrocarbon gases is the gaseous product of decarburization.

Metallic impurities would diffuse to the surface of a solid very much more slowly than interstitial impurities, and only those impurities with low boiling points and/or those that can combine with another element to form gaseous compounds can be liberated at the surface at a reasonable rate. Solid-state refining, then, is not generally a satisfactory means of removing metallic impurities from molybdenum.

Thermodynamic calculations cannot be used to predict a theoretical limit for purification of molybdenum because activity data for dilute solutions of carbon, hydrogen, oxygen, and nitrogen in molybdenum are unavailable. There is, however, a thermodynamic basis for assuming that the presence of MoO_2 and/or Mo_2N would not prevent solid-state purification in vacuo at high temperatures. The free energy of formation of Mo_2N is positive at temperatures above about 900 F. The dioxide of molybdenum is considerably more stable than the nitride, but a plot of calculated dissociation pressures for MoO_2 as a function of temperature, Figure 1, indicates that, when the partial pressure of oxygen is 0.76 μ Hg, MoO_2 begins to become unstable at about 3200 F. Therefore, at higher temperatures and/or lower pressures, MoO_2 would become increasingly unstable. The rate of the dissociation, however, cannot be predicted from thermodynamic principles.

EXPERIMENTAL MATERIAL

The solid-state purification experiments were carried out on unalloyed molybdenum sheet stock. The sheet, which was rolled from arc-cast Climax Heat 2312-A, was 0.137-inch thick and contained 0.019 percent carbon. Ten mills were ground off from each side, and specimens 3.5 in. x 0.277 in. x 0.115 in. were made.

APPARATUS

Description

An all-glass, high-vacuum system was designed and constructed for conducting experiments on the solid-state refining of the molybdenum specimens. A detailed description of the function of the various parts of the apparatus was presented in Reference 4. A photograph of the unit is shown in Figure 2 of the present report. After the photograph was taken, three additions were made. A second coaxial power cable was installed in parallel with the first cable to reduce I^2R -type heating of the cables. A small glass tube containing a fine capillary constriction was connected to the system as a side arm on the access tube to permit controlled introduction of gaseous atmospheres into the purification chamber. Finally, a gas sampler was connected to the vacuum line between the diffusion pump and the mechanical pump so that gases being pumped out of the purification chamber could be collected for chromatographic analysis.

The interior of the purification chamber is shown schematically in Figure 3. This drawing is essentially self-explanatory. The induction coil consisted of a helix containing 35 turns of 3/16-inch copper tubing with an inside diameter of 2.5 inches and a length of 8.5 inches. It was found that this coil could be operated while immersed in tap water without insulation on the coil, provided that the only contact between the coil and ground was the tap water. The purpose of the susceptor, of course, was to utilize more of the total available magnetic field for generating heat than the specimen could alone. Essentially, all of the induction heating occurred in the susceptor, and the specimen was heated mainly by radiation from the susceptor. It was established in preliminary experiments that without a susceptor, molybdenum specimens of the size used in this study could not be heated to incandescence with a 2.5-inch diameter induction coil and the 4200 cps power source available.

Figure 4 shows schematically the arrangement used for the controlled introduction of gaseous atmospheres into the purification chamber. The transition from copper to pyrex tubing was effected by a special Kovar-to-pyrex seal, with the Kovar being silver soldered to the copper. All of the pyrex members were connected by glass-blowing techniques. The entire system was checked for leaks with a helium leak detector. During a purification run, the mercury level in the manometer (lower left, Figure 4) was above the stopcock, leaving the needle valve and connections in the copper line as the only possible leakage points. These points were periodically tested for leaks with a helium leak detector.

The study of solid-state refining in gaseous atmospheres centered around the use of ultrapure hydrogen. The pure hydrogen was obtained by passing ordinary tank hydrogen through a palladium-diffusion purifier. The purity of the hydrogen was tested chromatographically on a sample taken at the downstream side of the needle valve. No impurities were detected. For the given chromatograph and sample size, this was interpreted to mean that the hydrogen contained not more than 1 to 2 ppm impurities by volume.

Operating Characteristics

Data pertaining to the operation of the apparatus are listed below:

Maximum attainable temperature	4000 F
Ultimate pressure at 4000 F	2×10^{-7} mm Hg
Power output of the 4200 cps generator to maintain specimen at 4000 F	11 KW at 190 V
Heating time from room temperature to 3000 F	Approximately 10 min.
Cooling time from 3600 F to 1550 F	5.4 min.
Temperature difference between specimen and susceptor	Approximately 150 F at 3600 F

To ascertain the temperature variation along the length of the 3.5-inch specimen, steps were ground on one specimen, as shown in Figure 5, so that optical temperature measurements could be taken at five positions including the lower end. The results, also presented in Figure 5, indicated that the cooling of the ends of the specimen due to radiant heat losses was not intolerable and, as anticipated, was more pronounced at higher temperatures.

EXPERIMENTAL PROCEDURES

Specimen Preparation

Strip specimens 3.5 in. x 0.277 in. x 0.115 in. were prepared from the 0.137-inch thick sheet stock by sawing and surface grinding operations. The final 0.002 inch was removed in the course of hand polishing one side of each specimen through 3/0 abrasive paper. The polishing was done prior to annealing so that hardness and bend tests could be performed after annealing with full assurance that the surface of the specimens would be completely free from work-hardened material.

The specimens were annealed one hour at 2500 F in a vacuum somewhat better than 0.1μ Hg. Later, after it was found that considerable grain coarsening occurred during the solid-state refining treatments, four specimens that had been annealed at 2500 F were reheated to 3800 F for 1/2 hour to produce a grain size similar (approximately one mm average grain diameter) to that of the purified specimens. The condition of specimens annealed only at 2500 F is referred to in the report as "Base Condition No. 1", and the condition of specimens annealed at 2500 F plus reheated to 3800 F is referred to as "Base Condition No. 2".

Hardness Determinations

Vickers diamond pyramid hardness values were determined for each condition at room temperature, -106 F, and -321 F, using a 30 kg load. The temperature-control media for tests at -106 and -321 F were dry ice in alcohol and liquid nitrogen, respectively. The indentations were carefully positioned to avoid interference with bend tests which were to be run later on the same specimens. Values from a minimum of three impressions were averaged for each determination.

Bend Testing

The temperature of transition from ductile-to-brittle behavior in a bend test was used as a measure of ductility. Each strip specimen was cut into three one-inch long bend specimens. Tests below 400 F were run in a constant-temperature oil bath, and tests at 400 F or above were carried out in air in a small, resistance-heated furnace. The bend-test jig had a span of 1/2 inch, the radius of the tip of the ram was 0.10 inch, and the ram was moved by the crosshead of a Rhie tensile testing machine at a rate of 0.1 inch per minute. The maximum bend angle was 166°; the transition temperature was arbitrarily based on a 120° bend at fracture. The polished side of each specimen was made the tension side.

Solid-State Purification in a High Vacuum

Treatments under high-vacuum conditions were, with one exception, carried out before the apparatus was modified for use with gaseous atmospheres. Prior to the modification, the best vacuum ever attained was 2×10^{-7} mm Hg; after modification, the best vacuum that could be attained was 1×10^{-6} mm Hg. The difference probably was due to a very slow rate of outgassing of the new part of the apparatus through the fine capillary constriction (Figure 4).

Access to the purification chamber was gained through the top of the access tube (Figure 2) which was opened and resealed by glass-blowing techniques. The specimens were suspended in the center of the purification chamber by means of a hook made from 1/8-inch diameter molybdenum wire. The molybdenum hook in turn was hung on a Vycor cross member which was an integral part of the Vycor chamber. The possibility of accidental stressing of the specimen was eliminated by this method of support. The molybdenum hook could accommodate two specimens simultaneously.

Outgassing at the beginning of each run was achieved by heating the system upstream from the main cold trap (item 2, Figure 2) by means of a hot-air gun. The heating was continued for 1/2 hour while the diffusion pump and cold traps were in operation. For operation under high-vacuum conditions, liquid nitrogen was used in both cold traps. Pressure measurements were made with a CVC-VG1A hot cathode ionization gage (item 8, Figure 2) located between the purification chamber and the main cold trap. It was necessary to outgas the gage head by gentle heating with a flame from a Bunsen burner before reproducible readings could be obtained. Adequate heating of the gage was not possible with the hot-air gun because the insulation on the lead wires would have been damaged. Heat from a Bunsen flame was sufficiently localized that damage to the wires could be avoided.

Specimens were heated slowly enough that the pressure never exceeded 10^{-3} mm (1.0 μ) Hg. After the desired temperature was reached, as indicated by an optical pyrometer, it was observed that the pressure decreased at a decreasing rate.

The mercury cutoff (item 3 in Figure 2) was included in the system so that the purification chamber could be isolated from the pumps. The main reason for using the cutoff was to determine whether or not the combination of hot molybdenum vapor in a chamber with cool walls would act as an ion pump and produce better vacua than could be attained with the diffusion pump. This possibility was tested during one run when the temperature of the specimen was about 3950 F and the pressure was 5×10^{-7} mm Hg. The pressure increased slowly to a value of 2×10^{-6} mm Hg during the 10 minutes that the system was isolated. The obvious conclusion to be drawn was that if any pumping action was occurring in the chamber, it was not as effective as that of the diffusion pump.

Solid-State Purification by Solid-Gas Reactions

The initiation of a purification run involving a gaseous atmosphere was nearly identical to the procedure used to start a high-vacuum run. The difference was that that part of the apparatus which was upstream from the capillary constriction (Figure 4) was first evacuated and outgassed by heating with the hot-air gun and pumping through the multipurpose tube (lower left, Figure 4) with an NRC two-stage mechanical vacuum pump. For runs using wet hydrogen, freshly-boiled distilled water was introduced into the bubbler through the multipurpose tube. Finally, the three-way stopcock at the bottom of the multipurpose tube was turned to admit mercury from a leveling bottle. The purpose of the mercury was to prevent any leakage at the stopcock and to act as an open manometer for determining the pressure of the gas upstream from the capillary. Pressures from 1 to 1500 mm Hg absolute could be measured with this setup.

Admission of the gas to the system was then effected simply by opening the needle valve until the desired pressure was indicated by the manometer. The flow rate of the gas was governed by the pressure of the gas above the capillary; the pressure was controlled with the needle valve. Actual flow rates were not determined.

The pressure of the gas in the purification chamber was monitored by a thermocouple vacuum gage (item 9 in Figure 2). Since the gage was calibrated for air, the actual pressures for other gases were not known. In order to operate the purification chamber at "indicated pressures" above 30 μ Hg, it was necessary to turn off the diffusion pump. Also, to permit analysis of exhaust gases containing CO and other gases that would condense at -321 F, dry ice and alcohol were substituted for liquid nitrogen in the cold traps. It was not possible to analyze for water vapor with the gas chromatograph that was used.

Metallographic Evaluation

Metallographic techniques were used as an aid in determining the extent of purification insofar as precipitated phases were involved. For detecting small amounts of precipitated phases, intergranular surfaces exposed by fracturing the specimen were examined at a magnification of 2000 diameters. This technique was supplemented by examinations of electropolished cross sections.

EXPERIMENTAL RESULTS

Solid-State Purification in a High Vacuum

The first specimen treated in a high vacuum was incidentally heated several times to temperatures in the range of 2000 to 3000 F in the course of arriving at a suitable induction coil design. The final treatment consisted of heating to approximately 4000 F over a period of 1.33 hours and holding at temperature for 5.5 hours. The pressure during the heat-up period ranged from 2.3×10^{-5} to 3.6×10^{-6} mm Hg. During the period of holding at 4000 F, the pressure dropped to a value of 2.5×10^{-7} mm Hg within two hours and to 2.0×10^{-7} mm Hg by the end of the 5.5-hour period.

When the specimen was removed from the apparatus, it was found that a large amount of molybdenum from the susceptor had vaporized and deposited on the specimen. The deposit was thickest at the center where the specimen thickness had increased from 0.115 inch to 0.150 inch and the width had grown from 0.277 inch to 0.316 inch. Some mass transfer of this type had been anticipated, but the extent to which it occurred was unexpected. The excessive mass transfer revealed a rather serious limitation of the apparatus, namely, that operation at temperatures near 4000 F for prolonged periods would contaminate the specimen, alter its shape, and, in time, destroy the susceptor. At the outset of the investigation, it was anticipated that purification temperatures approaching the melting temperature of molybdenum would be required to produce a high degree of removal of interstitial impurities.

The alteration of the specimen made it impossible to obtain meaningful hardness and bend test data for the vacuum-treated condition. The surface of the specimen was rough, each grain exhibiting many facets parallel to a specific set of equivalent crystallographic planes. The individual facets had smooth, lustrous surfaces, and most of them contained carbides that precipitated on the free surface apparently to about the same degree that precipitation on internal grain boundaries occurred. Photomicrographs showing carbide precipitation on the surface of the vacuum-treated specimen are presented in Figure 6. Figure 7 shows micrographs of (7A) a grain boundary exposed by an intergranular fracture, and (7B) a polished cross section of the same specimen. The area shown in Figure 7B was in the layer of vapor-deposited susceptor material near the edge of the specimen. The void in Figure 7B associated with precipitation of molybdenum carbide was typical of many voids observed in the vapor-deposited layer. The amount of carbide in the core of the specimen appeared to be the same as in the vapor-deposited layer, indicating that little or no difference in carbon content existed between center and surface.

A microhardness (20 g load) traverse was taken on an electropolished cross section to determine whether the vapor-deposited molybdenum was significantly different from the core or specimen material with respect to metallic impurities. The microhardness data are presented in Figure 8. The average hardness of the core was not significantly different from that of the deposited material, indicating that there was no gross contamination from the susceptor material.

Hardness determinations could not be made on the rough surface of the vacuum-treated specimen; therefore, hardness values were obtained from an electropolished cross section. They indicated an average hardness of 172 DPH (30 kg), to be compared with 168 DPH (30 kg) prior to the high-vacuum purification treatment. The carbon contents of the vacuum-treated specimen and an untreated specimen were determined from chips machined from the cross section. The analyses indicated that the carbon content had increased from 0.019% to 0.027% by weight. The carbon pickup from the susceptor was accepted as the most likely explanation for the marginal increase in hardness. The fact that the carbon which evaporated from the susceptor condensed on the specimen demonstrated that carbon cannot be removed from low-oxygen molybdenum as easily as the common gases.

Purification of Molybdenum Reaction Chamber Components

The high-vacuum purification treatment, which probably only purified the molybdenum with respect to the common gases, clearly demonstrated the need for purifying the apparatus with respect to carbon before the study could be continued.

Wet Palladium-Diffused Hydrogen: The first attempt to decarburize the molybdenum components in the high-temperature chamber was carried out with a wet, palladium-purified hydrogen atmosphere at reduced pressures. No CO or hydrocarbon gases could be found by chromatographic analysis of the gases pumped out of the reaction chamber, so the use of wet hydrogen was discontinued. The failure of wet hydrogen to effect measurable decarburization was assumed to be due primarily to the fact that the total pressure in the chamber was only about 1 mm Hg absolute. The apparatus was not operated at hydrogen pressures approaching full atmosphere because of the likelihood that the flowing hydrogen, being an excellent heat transfer medium, would cause the "O" ring seal between the water jacket and the glass chamber to become overheated.

Air, Dry Palladium-Diffused Hydrogen, and Vacuum: The second approach used to purify the molybdenum susceptor and heat shields was to oxidize the carbon to carbon monoxide in a reduced-pressure air atmosphere, and then deoxidize the molybdenum with dry, palladium-purified hydrogen. It was assumed that any nitrogen absorbed by the molybdenum during the air treatment could be removed with a subsequent vacuum treatment. The decarburization with air was carried out in two stages: (a) a 15.5-hour period of air charging at 3100 F and 45 to 90 μ Hg indicated air pressure, followed by (b) a 64.3-hour period at 3200 to 3600 F with the needle valve closed. The air flow was stopped before the temperature was raised above 3100 F to prevent the outer, cooler heat shields from becoming oxidized to the extent that they could not be properly reduced by subsequent hydrogen treatments.

It was anticipated that during stage (b), the use of higher temperatures would permit the absorbed and adsorbed oxygen to react with carbon, resulting in a more nearly complete removal of carbon than could be realized at lower temperatures. Chromatographic analyses of exhaust gases confirmed that decarburization occurred during stage (b). One analysis early in stage (b) showed that 81.6 percent of the exhaust gas was CO. An analysis at the end of stage (b) indicated that no CO was present in the reaction chamber.

At the completion of stage (b) of the oxidation treatment, a specimen which had been placed in the reaction chamber for monitoring purposes was removed for examination. The surface of the specimen did not have a metallic luster, presumably because of a thin oxide surface layer. A 1/2-inch length was cut from the lower end of the specimen for metallographic examination, and the remaining part was returned to the apparatus for the deoxidation treatment.

A comparison of Figure 9 with Figure 10 illustrates the effectiveness of the oxidation treatment in reducing the carbon content to below the limit of solid solubility. The actual carbon content was not determined at this point, but the absence of carbides indicated that the molybdenum contained less than 0.004 percent carbon. As expected, the treatment in air raised the oxygen content of the molybdenum to above the solid solubility limit. This is evidenced by the small specks of oxide visible in both micrographs of Figure 10. The occurrence of the larger particles seen in Figure 10A was unexpected. They were present only in a narrow zone parallel with the surface. The zone started at the interface between the original specimen and a thin layer of vapor-deposited molybdenum and extended inward for about two mils. The fact that the particles were formed in conjunction with the treatment in air suggested that they might be nitrides. Later, this view was strongly supported by the observation that similar precipitates were not present after a decarburization treatment employing tank oxygen instead of air. This matter will be discussed later in the report.

To complete the purification of the molybdenum components in the purification chamber, a run was made with dry, palladium-diffused hydrogen at 3200 F for 42 hours. Metallographic examination of the monitor specimen after the run revealed that the molybdenum had been deoxidized to the extent that no oxide cracks could be found at a magnification of X2000 on either an electropolished cross section or on grain boundaries exposed by an intergranular fracture. Photomicrographs of this specimen are presented in Figure 11. The precipitates thought to be nitrides (Figure 10A) apparently were unaffected by the deoxidation treatment (Figure 11R). The random spots seen in Figure 11A are believed to be micropores.

The purifying effect of the air and dry hydrogen treatments was also evident in room-temperature hardness values taken on the surface of the monitor specimen. The hardness after the hydrogen treatment was 160 DPH (30 kg) -- 8 DPH units lower than the initial value of 168 DPH. It was assumed that the molybdenum components of the reaction chamber underwent purification and softening to a degree similar to that experienced by the monitor specimen.

A final vacuum treatment was given to the monitor specimen to ascertain whether or not residual hydrogen from the hydrogen treatment was influencing hardness. The vacuum treatment consisted of heating at 3250 F for 66 hours and 3600 F for 2.25 hours in a vacuum of 3×10^{-6} to 1×10^{-6} mm Hg. The hardness of the specimen remained unchanged at 160 DPH (30 kg). A secondary purpose of the vacuum treatment was to test the thermal stability of the precipitates believed to be nitrides (Figures 10A and 11B). The precipitates were still present after the treatment. The only apparent effect of the vacuum treatment was to broaden the zone in which the precipitates were located, and to cause the dispersion of the particles to become finer on the side of the zone nearer the center. The change in dispersion is illustrated by the fractographs in Figure 12.

The carbon content of the monitor specimen was determined by analysis of chips machined from the cross section. The analysis indicated that the carbon content was 0.003 ± 0.001 percent by weight.

Solid-State Purification in Oxygen and Palladium-Diffused Hydrogen

Briefly, the research up to this point had demonstrated that (a) removal of carbon from low-oxygen molybdenum cannot be accomplished by heating to 4000 F in a high vacuum, (b) carbon can be reduced to a level below its limit of solid solubility in molybdenum by heating to 3100 to 3600 F in about 50 μ Hg of air, (c) the oxygen absorbed by the molybdenum during oxidation of the carbon can be removed by treatment in dry, palladium-diffused hydrogen, and (d) a final vacuum treatment applied to decarburized plus deoxidized molybdenum produces no additional purification as judged by hardness determinations. It was concluded from these results that probably the best procedure for effecting purification of molybdenum in the solid state would be a duplex treatment consisting of controlled oxidation to remove carbon, followed by deoxidation to remove oxygen. However, in view of the problem of the unidentified precipitate that formed in conjunction with the decarburization treatment in air, it appeared that relatively pure oxygen ought to be substituted for air in the oxidation step. If the precipitate were a nitride, the use of oxygen would eliminate the problem.

Decarburization in Oxygen: Two strip specimens were treated together in a flowing atmosphere of commercially-pure oxygen at reduced pressures. The treatment was carried out in two stages. In the first stage the specimens were charged with oxygen by heating to 2200 F for one hour and 2800 F for one hour at an average indicated oxygen pressure of 50 μ Hg. To initiate the second stage, the flow of oxygen was stopped. This allowed the pressure to decrease to 2 μ Hg. The specimens were then heated to 3000 F for 16 hours and 3250 F for 20 hours. At this point, the specimens were removed from the apparatus for visual and metallographic examination.

The surface of the specimens was dull in appearance, like the monitor specimen treated in reduced-pressure air. A 1/2-inch long piece was cut from the end of one specimen, and the two specimens were returned to the chamber for deoxidation in reduced-pressure hydrogen. The microstructure of the oxygen-decarburized molybdenum, typified in Figure 13, was similar to the air-decarburized molybdenum with one important exception. There were no precipitates like those seen in Figures 11B and 12A. This observation was interpreted as near-proof that the unidentified particles in the air-treated specimen were nitrides, despite their apparent high stability in vacuo at high temperatures. This will be discussed later.

Deoxidation in Palladium-Diffused Hydrogen: The specimens were finally treated in dry, palladium-diffused hydrogen to remove oxygen. The deoxidation treatment was 67.5 hours in duration, and it was all at 3050 F. The pressure was estimated to be about 1 mm Hg.

Evaluation of Purified Molybdenum

It was assumed that the purification effected by the treatments in reduced-pressure oxygen and hydrogen atmospheres approached the maximum possible with the given apparatus. The effectiveness of the solid-state purification was evaluated by means of four different comparisons between purified and non-purified material. The comparisons were based on (a) microstructure, (b) carbon content, (c) hardness at -321, -106, and 76 F, and (d) temperature of transition from brittle-to-ductile behavior in a bend test.

Microstructure: The purified specimens were examined metallographically at a magnification of X2000, and no precipitates were found. Typical photomicrographs of the purified molybdenum are presented in Figure 14. The black spots visible in the fractograph (Figure 14A) were thought to be micropores, although no direct evidence was available to support the idea. The structure prior to purification was as shown in Figure 9.

Carbon Content: The original chemical analysis of the arc-cast ingot from which the specimen sheet stock was rolled gave a carbon content of 0.021 percent. An analysis of the material after fabrication into a strip specimen and after being recrystallized in vacuo at 2500 F indicated a carbon level of 0.019 percent. After the solid-state purification treatments in oxygen and hydrogen at reduced pressures, the carbon content was found to be 0.003 ± 0.001 percent. The same carbon level was found in the monitor specimen that had been treated successively in reduced-pressure air, reduced-pressure hydrogen, and in a vacuum.

These data can be compared with the results of a decarburization treatment in low-pressure, flowing oxygen which was carried out at the Battelle Memorial Institute. (1) In that instance, the specimen, a 1/4-inch diameter rod, was resistance heated to 3000 F and held for 16 hours in an oxygen pressure of 10 to 20 μ Hg, and then vacuum annealed nine hours at 3800 to 4000 F. That duplex treatment reduced the carbon level to 0.008 percent from an initial value of 0.059 percent. Small precipitates believed to be carbides were observed on grain boundaries, exposed by intergranular fractures, in the purified rod. No carbides were visible in fractures of molybdenum purified in the present investigation.

Hardness: Hardness data for molybdenum purified in oxygen and hydrogen are presented in Figure 15. In the same figure are plotted data for material given no purification treatment. The softening effect of the solid-state purification was rather small, so it was decided to treat the data statistically to help clarify their significance. The calculated statistical parameters included means, unbiased estimates of the standard deviations, and 95 percent confidence ranges for the means. The results of the calculations are summarized in Table 1, and a detailed sample calculation is given in the Appendix.

First of all, the calculations demonstrated that the 9.6 DPH decrease in mean hardness produced by the purification treatment was significant, even if it was not spectacular. Secondly, the data showed the importance of proper surface preparation. A comparison of the mean hardness values for States 1, 2, and 3 in Table 1 shows that significantly lower values were obtained when the recrystallization anneal was given after the surface was polished. When the recrystallization anneal preceded the preparation of the surface, the hardness values were 10 DPH units higher, even though the surface was electropolished. The data for States 1 and 2 (Table 1) showed that electropolishing for 40 seconds did not remove enough metal to even partially eliminate surface hardening caused by manual polishing on abrasive papers. It ought to be pointed out that the coarse grinding which was done after recrystallization was carried out with techniques commonly used for steel specimens. Check tests indicated that hardness values below 170 DPH could be obtained for States 1 and 2 when special grinding procedures were employed.

Finally, the hardness level and the variability or scatter of the data were found to depend upon the observer. Differences between average hardness values for State 3 in Table 1 were, no doubt, caused by systematic differences in judgment on measuring diagonals of indentations. Using the estimated standard deviation, S_H , in Table 1 as a basis for comparing data scatter, it can be seen that differences between observers (State 3, Table 1) were small in comparison with differences due to other unidentified factors (data from Observer A for States 2 and 3, Table 1). No single factor such as grain size, carbide morphology, surface preparation, hardness level, or total number of impressions averaged could be used to explain the differences in data variability. The only possible correlation appeared to be that carbide-containing specimens with stress-free surfaces (States 3 and 4, Table 1) gave data with a greater degree of scatter than specimens that were either carbide-free (State 5, Table 1) or which had surfaces hardened by improper preparation (States 1 and 2, Table 1).

Bend Ductility: The effect of solid-state purification on ductility was evaluated by comparing curves of fracture bend angle versus temperature for purified and nonpurified molybdenum. The temperature of transition from ductile-to-brittle behavior was established for nonpurified molybdenum in Base Condition No. 2 and for molybdenum purified in reduced-pressure oxygen and hydrogen atmospheres. The results, shown in Figure 16, demonstrated that the removal of oxides and carbides from the microstructure, as determined by observations at X2000 (compare Figures 9 and 14), produced no improvement in ductility. In fact, the purified molybdenum appeared to have a ductile-to-brittle transition temperature about 25 F higher than that of nonpurified molybdenum.

These results were rather surprising. They seemed to suggest that 0.003 percent carbon can cause as much or more embrittlement in the form of dissolved carbon concentrated* at grain boundaries as can 0.019 percent carbon which precipitates mainly as carbides at the grain boundaries. However, the two conditions studied might not have been equivalent with respect to microporosity. If the purified material contained more microvoids than the nonpurified molybdenum, this difference might explain why the removal of carbides and oxides failed to improve the ductility.

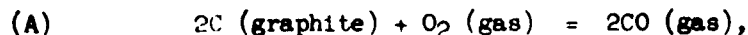
The transition temperatures based on a 120° bend at fracture were rather high, namely, 365 and 390 F. This was partly caused by the large grain size, the low ratios of specimen width to thickness and of ram point radius to specimen thickness, and perhaps also microporosity at grain boundaries.

DISCUSSION

General

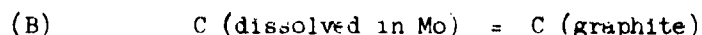
The objective of the present research was to determine the laboratory limits of solid-state purification reactions for unalloyed molybdenum. It is felt that this objective was met insofar as solid-gas reactions below 3600 F are concerned. This judgment, which refers only to interstitial purification, is based on two assumptions: (a) that oxygen and hydrogen are the best gaseous agents for solid-state removal of carbon and oxygen, respectively, and (b) that most of the total purification possible at the temperatures used was completed within the time periods used. The latter assumption is supported by the results of solid-state refining experiments conducted at the Battelle Memorial Institute.(1) In the Battelle experiments, which involved 1/4-inch diameter molybdenum rods vacuum treated at 3500 F, most of the total purification achieved in 24 hours occurred during the first three hours. In the present research, purification times were of the order of 100 hours at 3000 to 3250 F, excepting the high-vacuum treatment at 4000 F which was 5.5 hours in duration.

The present research probably was not successful in establishing the ultimate limits for solid-state purification of molybdenum. The main reason for this was that only relatively low purification temperatures were employed; operation at temperatures above 3600 F resulted in contamination of the specimen with vapors from the surrounding susceptor. The removal of carbon by oxygen probably would be enhanced significantly if temperatures above 4000 F could be used. This follows from the thermodynamics of the reaction,

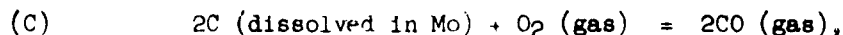


namely, that the change in standard-free energy, ΔF° , becomes more and more negative as the temperature is raised. In other words, the driving force for the reaction increases as the temperature is raised. The reverse is true for the formation of water vapor and the condensed oxides of metals. The only uncertainty as to the advantage of higher temperatures for decarburizing is that the free energy change for the reaction

* The concentration or segregation of dissolved carbon at grain boundaries was not demonstrated by the present research, but its occurrence is assumed on the basis of the generally accepted principle of equilibrium segregation.



is unknown. Since reaction (B) (multiplied by two) must be added to reaction (A) to give the decarburization reaction of interest,



the temperature dependence of the driving force, ΔF° , for reaction (C) cannot be predicted with any certainty. However, the proven effectiveness of carbon deoxidation during arc melting of molybdenum strongly suggests that the ΔF° for reaction (C) is not unfavorable, at least up to the melting point of molybdenum.

Unidentified Phase in Air-Decarburized Molybdenum

The unidentified precipitate (Figures 10A and 11B) that formed during decarburization of molybdenum in low-pressure (50 μ Hg) air was almost certainly a nitride. It was not present in another specimen after a similar decarburization treatment in which tank oxygen was substituted for air.

Two observations were made in connection with the precipitate which indicated that the nitride was not Mo_2N or MoN . First, the particles were not dissociated by a subsequent, prolonged anneal in vacuo. Both Mo_2N (6) and MoN (7) are known to be very unstable under these conditions. The second clue that the phase was not a molybdenum nitride was that, when first noticed, the particles were confined to a narrow zone near the original specimen surface. On subsequent exposure to high temperatures in vacuo, the band broadened slowly as if it were controlled by the diffusion of a metallic (substitutional) impurity into the specimen. If only nitrogen and molybdenum were involved, the inward diffusion of nitrogen would have been very rapid, and nitride particles would have precipitated throughout the cross section on cooling.

The initial localization of the nitride particles along the interface between the specimen and the layer of vapor-deposited material from the susceptor and the slow broadening of the nitride zone into the specimen suggested that the deposit might have contained an impurity capable of diffusing into molybdenum and forming a stable nitride. To check this possibility, qualitative spectrographic tests for titanium and zirconium, two strong nitride-forming elements, were made on an untreated molybdenum strip specimen and a molybdenum specimen bearing a thick deposit of molybdenum susceptor material. A TZM (Mo + 0.5% Ti + 0.08% Zr) alloy specimen was used as a basis for comparison. No trace of titanium or zirconium was found in the untreated molybdenum. The vapor-deposited molybdenum showed no zirconium, but definite lines from the titanium spectrum were found. The titanium lines were very weak in comparison to the titanium lines from the TZM alloy, but it was estimated that the concentration of titanium in the deposit could be as high as 0.1 percent by weight. Conceivably, that would be enough to produce the observed effects.

One apparent inconsistency in the hypothesis that the nitrides were TiN produced by contamination from the vapor-deposited layer is that nitrides were not observed in the titanium-containing layer itself. A possible explanation might be that the solid solubility of nitrogen was high enough in the titanium-bearing material that nitride precipitation did not occur. Another possibility is that nitrides were present in the outer layer, but in the form of a fine dispersion that was not resolved with the light microscope. Such a situation was reported by Mukherjee and Martin (8) who investigated the nitriding process in a Mo + 1.0% Ti alloy. Mukherjee and Martin reported that TiN particles were visible by light microscopy only near the advancing front of the diffusion layer. Near the surface, nitrides could be seen only with the aid of an electron microscope.

It is to be emphasized that the specimens on which the hardness and bend test data were taken for this report were not appreciably contaminated by susceptor material. The specimen temperature was kept low enough to hold the rate of mass transfer of susceptor material at a safe, low level. As an added precaution, the two specimens that were purified in oxygen and hydrogen were hung close together with their polished sides facing in. If any contamination occurred, it was on the backs and sides of the specimens where it could not affect the hardness or bend test results.

Comparison of Hardness and Bend Test Results with Published Data

There is a large volume of literature containing reports of research and development work on molybdenum. Much of the activity was and is directed toward finding methods for making molybdenum and its alloys more ductile. Hardness data are relatively sparse in the literature, presumably because the theoretical significance of hardness values is questioned by many metallurgists, and because hardness--being determined by a compression-type test--is not a good indicator of ductility. Nevertheless, there are enough hardness data available for high-purity molybdenum to permit a comparison with the present study.

Most of the available hardness data were taken at room temperature. The mean hardness of the molybdenum purified in the present study was 158.5 DPH. In general, the hardness reported in the literature for high-purity molybdenum ranges from 160 to 180 DPH (9, 10, 11). In two instances, hardness values as low as 150 to 151 DPH (10 kg) were determined on unalloyed molybdenum at the Climax laboratory (4). Usually the purity of the various lots of molybdenum tested was high, but not high enough to exclude minor-phase precipitates from the microstructure. Apparently this is relatively unimportant, provided the precipitates are not present in a fine dispersion. The present research demonstrated that the removal of grain boundary precipitates does not drastically reduce the hardness of molybdenum.

The most significant aspect of all the hardness data on refractory metals is that the hardness of molybdenum is far out of line with the hardness of some of the other body-centered cubic refractory metals of equivalent purity. Prime examples are tantalum and niobium, each of which exhibit a hardness below 100 DPH. The hardness of tungsten, about 300 DPH, is even more out of line. The fact that different refractory metals cannot be correlated with hardness indicates that either (a) hardness depends much more critically on purity in molybdenum and tungsten than it does in niobium and tantalum, or (b) defect structures* present after recrystallization produce a greater hardening effect in molybdenum and tungsten than they do in niobium and tantalum. It appears that research in both areas ought to be pursued.

The bend test results cannot be compared in a precise manner with published data because of differences in test conditions. The bend tests carried out in molybdenum research at the Battelle Memorial Institute (1) were similar to the present tests with respect to the geometry of the specimens and jig. Unfortunately, the test results for high-purity molybdenum were reported by Battelle as the temperature at which the bend angle at fracture was 4°. On this basis, it is not possible to decide whether the molybdenum purified in the present work was more ductile than the molybdenum tested at Battelle.

CONCLUSIONS

1. Solid-state purification of unalloyed molybdenum by consecutive treatments in flowing, reduced-pressure atmospheres of tank oxygen and palladium-purified hydrogen at 2200 to 3250 F resulted in
 - (a) a reduction in carbon content down to 0.003% from 0.019% by weight,
 - (b) the elimination of minor phases from the microstructure, as judged by observations at X2000,
 - (c) a drop in room-temperature hardness down to 158.5 DPH from 168.1 DPH (30 kg), and
 - (d) a slight rise in the 120°-bend transition temperature, up to 390 F from 365 F.
2. In the apparatus employed, the use of a molybdenum susceptor to achieve high temperatures by induction heating created an unexpectedly serious problem. Because the temperature of the specimen was 100 to 150 F lower than that of the susceptor, vaporized material from the susceptor condensed on the specimen. Some mass transfer of this type was anticipated, but the large extent to which it occurred was surprising. To minimize the mass transfer and attendant contamination during prolonged treatments, the specimen temperature was limited to 3250 F.

* Structures within the grains which involve vacancies, dislocations, and possible stacking faults.

3. As a consequence of the temperature limit imposed by the susceptor vaporization problem, the main objective of the investigation was not achieved. The objective was to determine the experimental limits of solid-state purification in molybdenum. The driving force for the removal of carbon by oxidation to carbon monoxide is greater at high reaction temperatures; therefore, it is supposed that the practical limit of solid-state decarburization was not established by the present research because experiments were limited to relatively low reaction temperatures.
4. The results of the present study demonstrated that removal of minor-phase precipitates from coarse-grained, recrystallized molybdenum does not necessarily improve its ductility. In this instance, it is suspected that the solution and removal of precipitates might have created microvoids at grain boundaries and, thereby, prevented an improvement in ductility.
5. The all-glass construction of the purification apparatus and the use of a high-capacity, three-stage, mercury diffusion pump with two liquid nitrogen cold traps gave the desired combination of a high vacuum (2×10^{-7} mm Hg) without carbonaceous vapors from pump oil or vacuum grease in the purification chamber. The glass-blowing operations involved in removing treated specimens and introducing new specimens were relatively simple and easy.

RECOMMENDATIONS

The following suggestions for future research can be made on the basis of the present investigation and other published research:

1. It is clear from the contamination problem encountered in the present research that future apparatuses designed for solid-state purification of refractory metals must be based on a method of heating which will cause the specimen to be hotter than its immediate surroundings.
2. The apparent ability of palladium-diffused hydrogen to effect thorough deoxidation of molybdenum after a decarburizing treatment in oxygen at a reduced pressure indicates that a duplex oxygen and hydrogen treatment of molybdenum in the liquid state might be a means for producing low-carbon, low-oxygen molybdenum. It is recommended that an investigation be carried out to explore the merits of using reduced-pressure oxygen and palladium-diffused hydrogen atmospheres in sequence during a floating-zone refining process.

3. The apparent impossibility of reducing the hardness of "pure" molybdenum to much below 150 DPH indicates a need for investigating factors other than chemical purity which might influence hardness and ductility. Defect structures involving vacancies (Schottky defects), dislocations, and possibly stacking faults could cause high hardness and low ductility. Transmission electron microscopy would be the best research technique that could be used for studying defect structures in molybdenum.
4. It is suggested that a study of the effect of microvoids on the ductility of molybdenum be carried out. The present research demonstrated that removal of minor-phase precipitates from unalloyed molybdenum by solid-state purification does not necessarily result in better ductility. Random spots seen at X2000 in fractographs of purified specimens were thought to be microvoids which could be acting as stress raisers and causing poor ductility. It is suggested that the number of microvoids might be significantly reduced by warm working the material and giving it a recrystallization anneal.

Table 1

Statistical Parameters from Hardness Data on Unalloyed Molybdenum Taken Before and After Solid-State Purification Treatment

State	Specimen History	Observer(s)	Specimen No(s)	Total No. of Impressions, N	Hardness DPH*	Estim. Std. Deviation, $s_H = \sqrt{\frac{\sum(H-H)^2}{N-1}}$
1	Surface Ground + Recrystallized at 2500 F in <u>vacuo</u> + Hand Polished through 3/0 Paper	A	1	14	174.57 \pm 1.10 ^b	1.91
2	State 1 + Electropolished 40 seconds	A	1	14	174.43 \pm 1.03	1.79
3	State Ground + Hand Polished through 3/0 Paper + Recrystallized at 2500 F in <u>vacuo</u>	A, B, C, and D } B A	3,4,5,6,7,8, and 9 } 3,4,5 and 6 5,6, and 9	54 18 20	165.89 \pm 0.97 167.22 \pm 1.64 163.80 \pm 1.42	3.53 3.30 3.04
4	State 3 + Grain Coarsened 12 hour at 3800 F in <u>vacuo</u>	A and B	10	12	168.08 \pm 1.98	3.12
5	State 3 + Purified in Solid State with Reduced Pressure O ₂ and H ₂ at 2200 to 3250 F	A	11 and 12	20	155.50 \pm 1.26	1.96

* Overall Mean Room-Temperature Hardness = 167

a The number multiplied by 0.6745 gives the more familiar "probable error".

b Plotted figures in this column indicate 95% confidence band for means determined by the number, N, of impressions shown in adjacent column on the left.

c Reported to in the report as "Base Condition No. 1".

d Reported to in the report as "Base Condition No. 2".

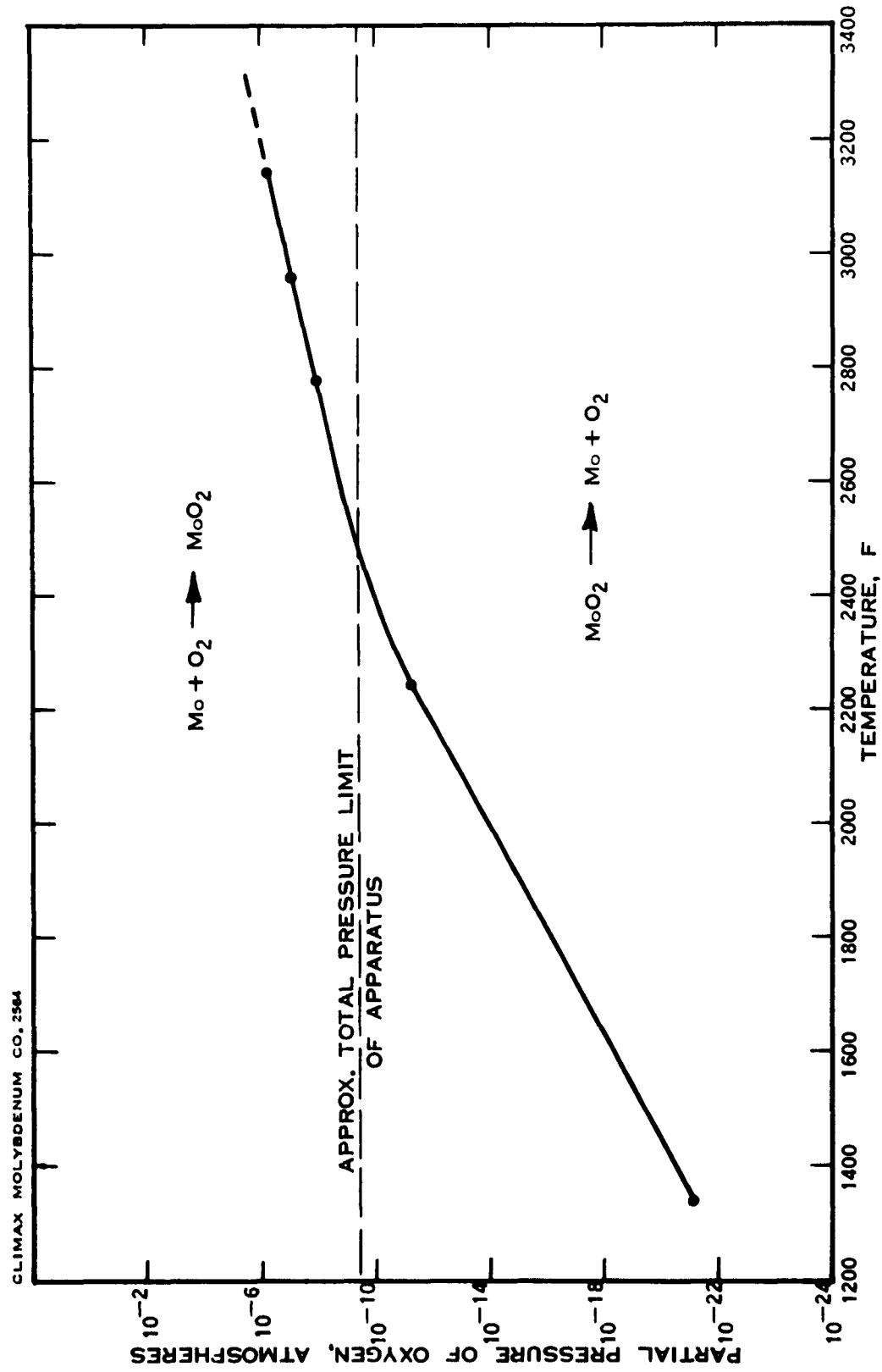


FIGURE 1 - EFFECT OF TEMPERATURE ON THE EQUILIBRIUM PARTIAL PRESSURE OF O₂ IN THE PRESENCE OF MoO₂ AND Mo. THESE DATA WERE CALCULATED FROM THE FREE ENERGY OF FORMATION DATA IN REFERENCE 3.

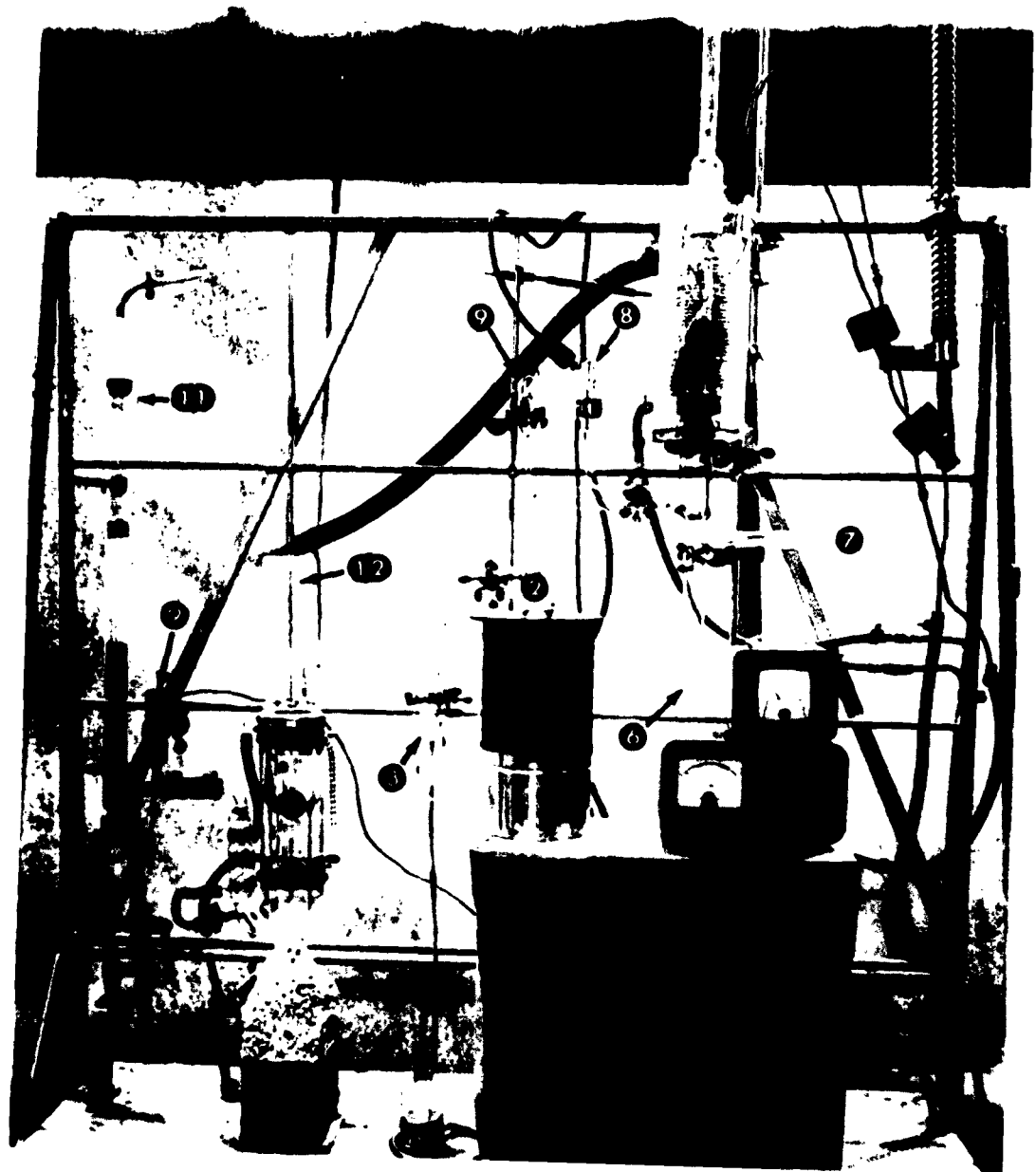


FIGURE 2 - SOLID-STATE PURIFICATION APPARATUS, Consisting of (1) Water-Cooled Vycor Heating Chamber with External Induction Coil, (2) Cold Trap, (3) Hg Cutoff, (4) Hg Pump, (5) Coaxial Power Cable, (6) Sight Window, (7) Shutter, (8) Ionization Gage, (9) Thermocouple Gage, (10) Access Tube, (11) Drying Column, and (12) Hg-Return Thimble.

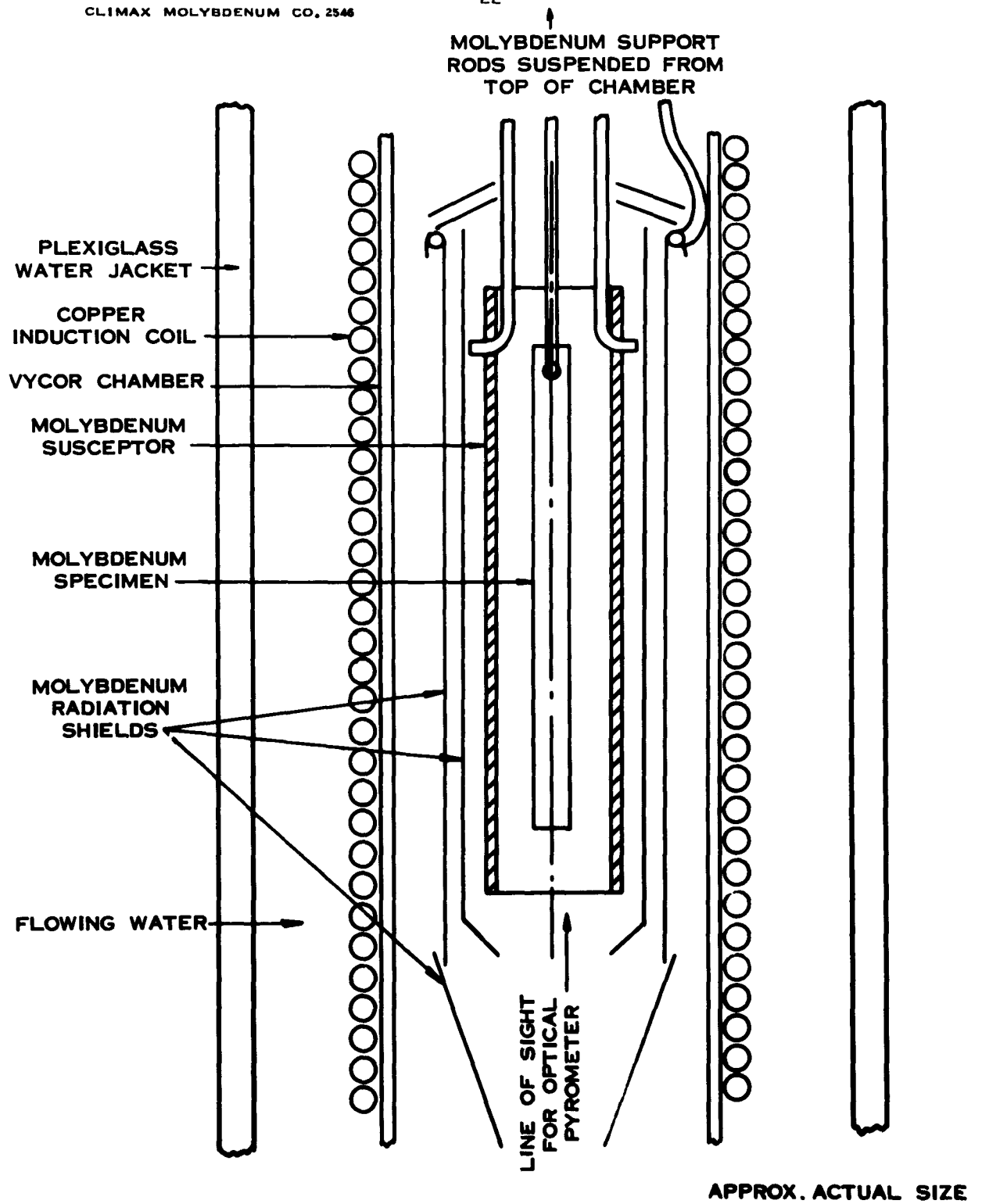


FIGURE 3 - SCHEMATIC DRAWING OF HIGH-TEMPERATURE
PURIFICATION CHAMBER

CLIMAX MOLYBDENUM CO. 2547

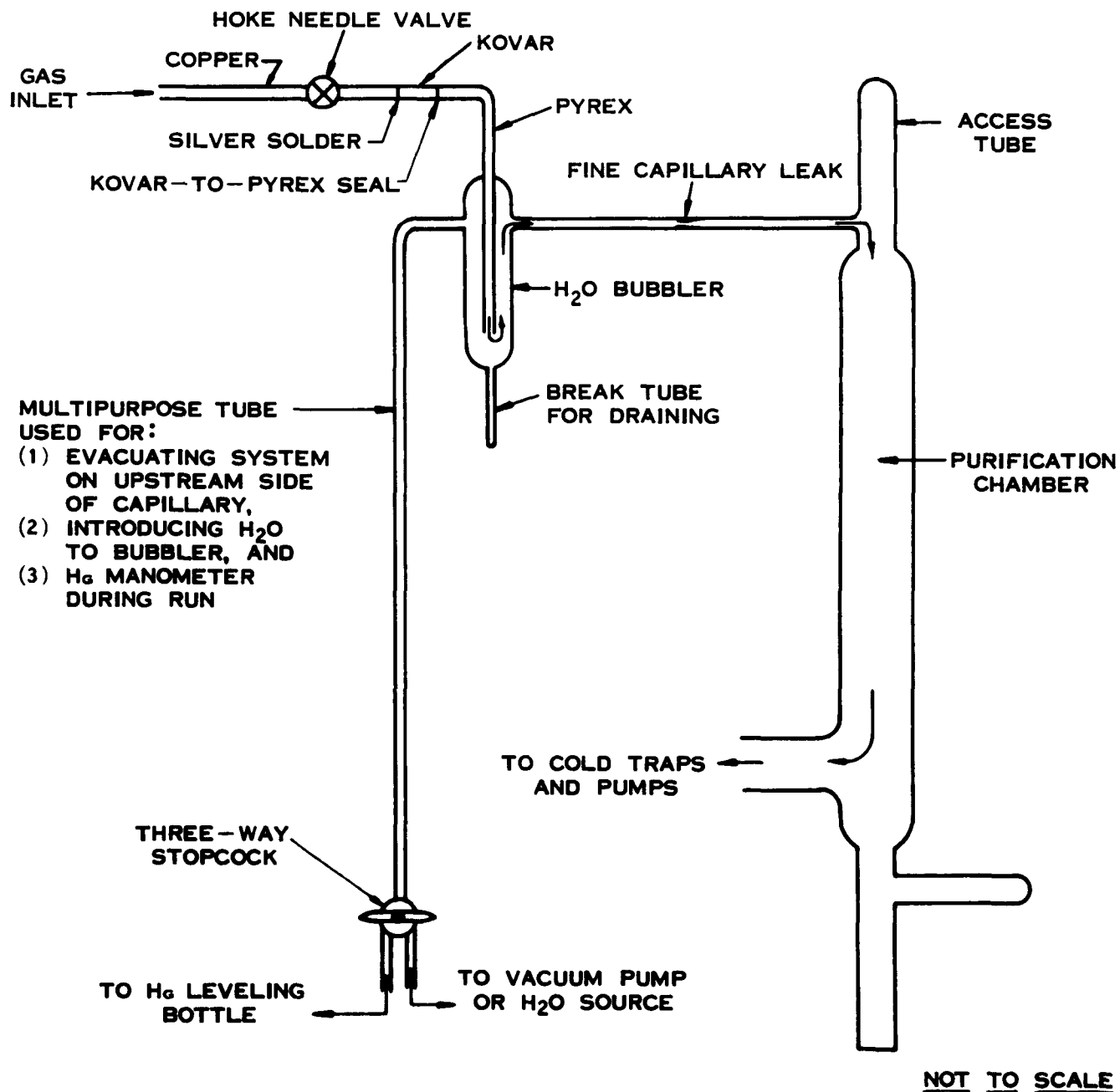


FIGURE 4 - SCHEMATIC DIAGRAM SHOWING APPARATUS USED FOR INTRODUCING GASEOUS ATMOSPHERES INTO PURIFICATION CHAMBER

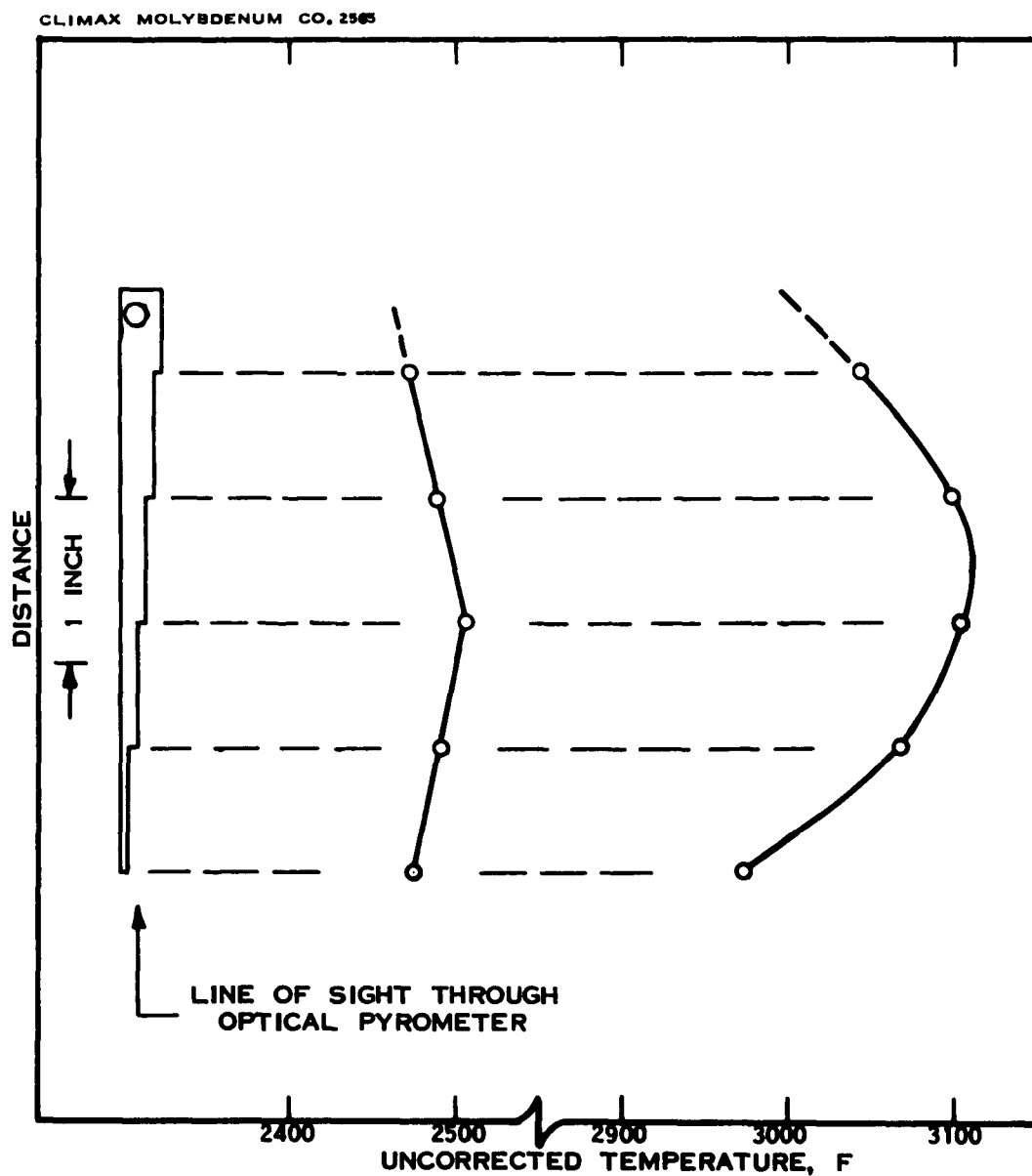


FIGURE 5 — TEMPERATURE GRADIENTS DETERMINED BY OPTICAL PYROMETER READINGS ON FACES OF A STEP SPECIMEN 0.115 INCH THICK

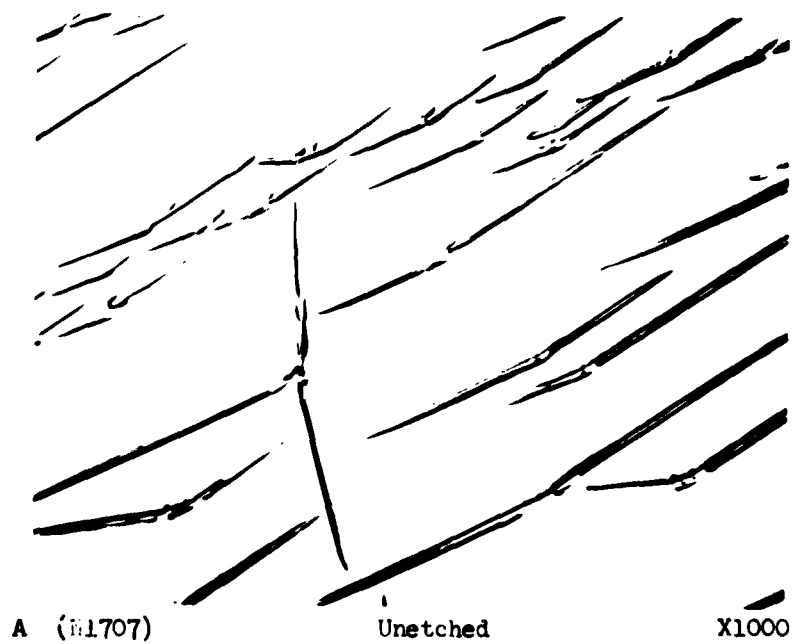


FIGURE 6 - Carbide Precipitates on Free Surface of Molybdenum
Heated in High Vacuum at 4000 F for 5.5 Hours



A (N1297)

Fractograph

X2000

B (N1299)

Electropolished Only

X2000

FIGURE 7 - Photomicrographs of Molybdenum Treated at 4000 F for 5.5 Hours in High Vacuum Showing (A) Carbides on Grain Boundary Exposed by Intergranular Fracture, and (B) Carbides in Polished Cross Section

CLIMAX MOLYBDENUM COMPANY 2587

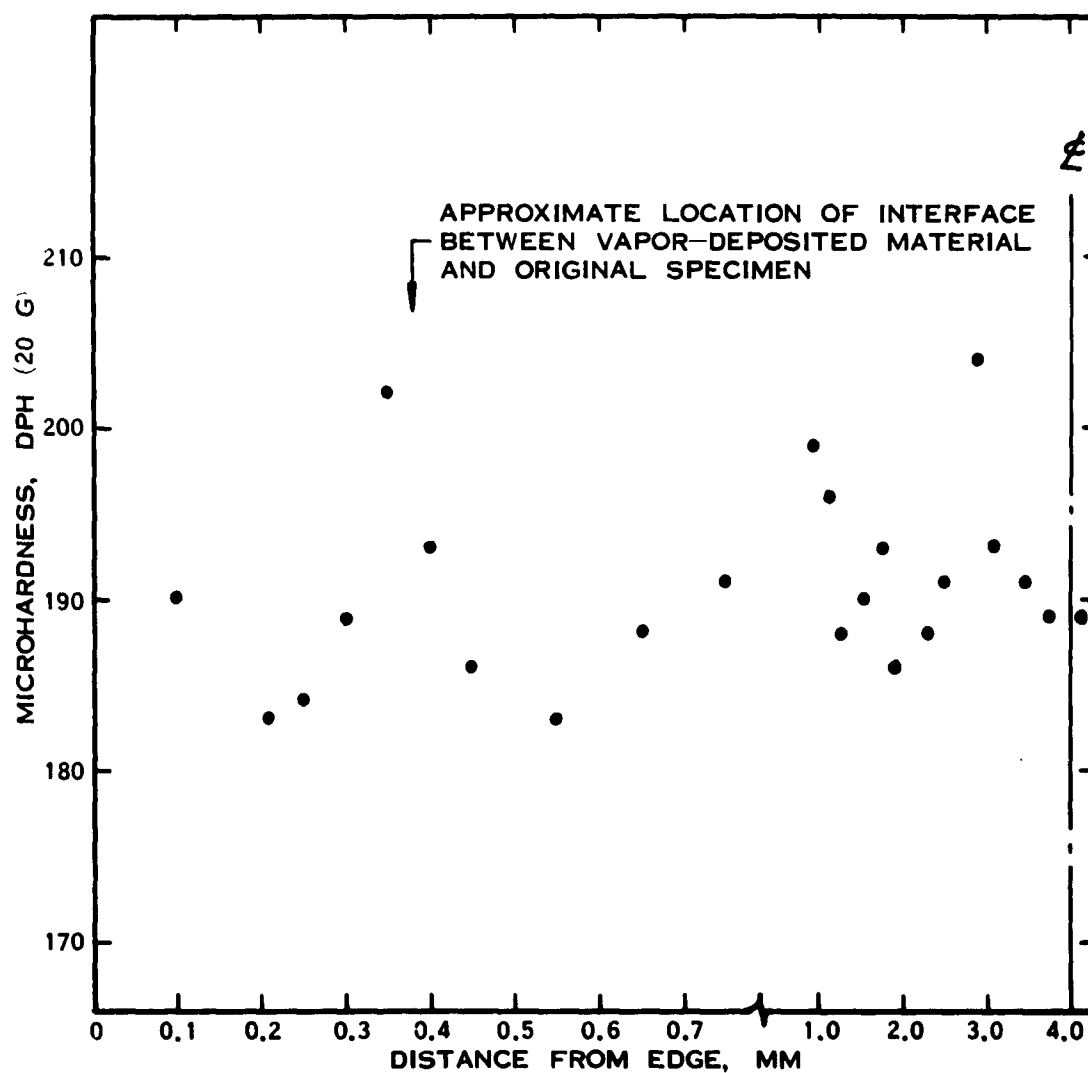


FIGURE 8 -- MICROHARDNESS TRAVERSE ON CROSS SECTION OF A MOLYBDENUM SPECIMEN AFTER TREATMENT IN HIGH VACUUM AT 4000 F. DURING THE TREATMENT, MOLYBDENUM FROM THE SUSCEPTOR WAS VAPOR-DEPOSITED ONTO THE SPECIMEN.



A (N1492)

Fractograph

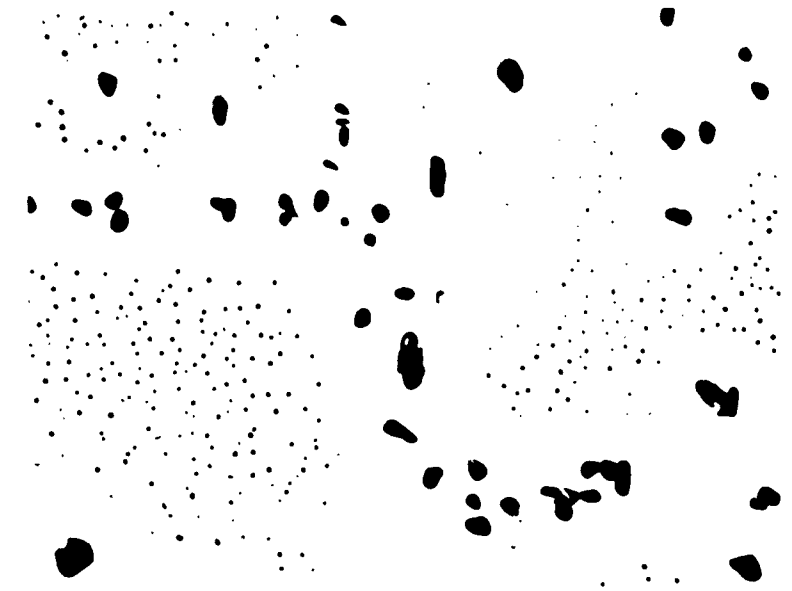
X2000

B (N1489)

Electropolished Only

X2000


FIGURE 9 - Microstructure of Unalloyed Molybdenum in Base Condition No. 2 as Revealed in (A) Grain Boundary Exposed by Intergranular Fracture, and (B) Electropolished Cross Section. Note the absence of oxide specks.



A (N1415) Fractograph Near Edge of Specimen X2000

B (N1460) Electropolished Only, X2000
Center of Cross Section

FIGURE 10 - Unalloyed Molybdenum After Treatment in About
50 μ Hg Air at 3100 to 3600 F for 79.8 Hours.
Note absence of carbides and presence of small
oxide specks in both micrographs. Larger
particles in fractograph are presumably nitrides.



A (N1462) X2000 Fractograph Near Center of Specimen B (N1461) X2000 Fractograph Near Edge of Specimen

C (N1464) Electropolished Only, X2000
Center of Cross Section

FIGURE 11 - Microstructure of Same Specimen as in Figure 10,
but After Additional Treatment in Dry, Palladium-
Diffused Hydrogen at 3200 F for 42 Hours at
About 1 mm Hg Pressure

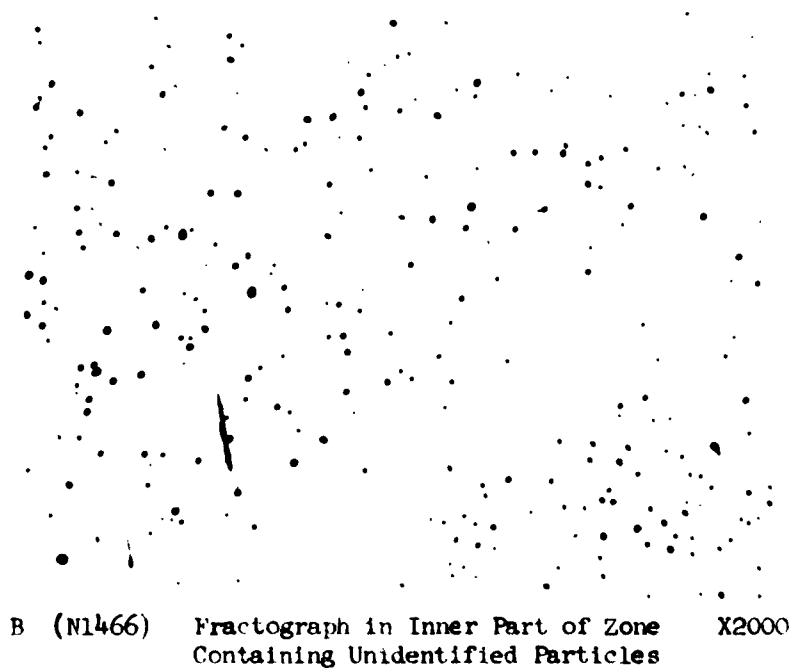
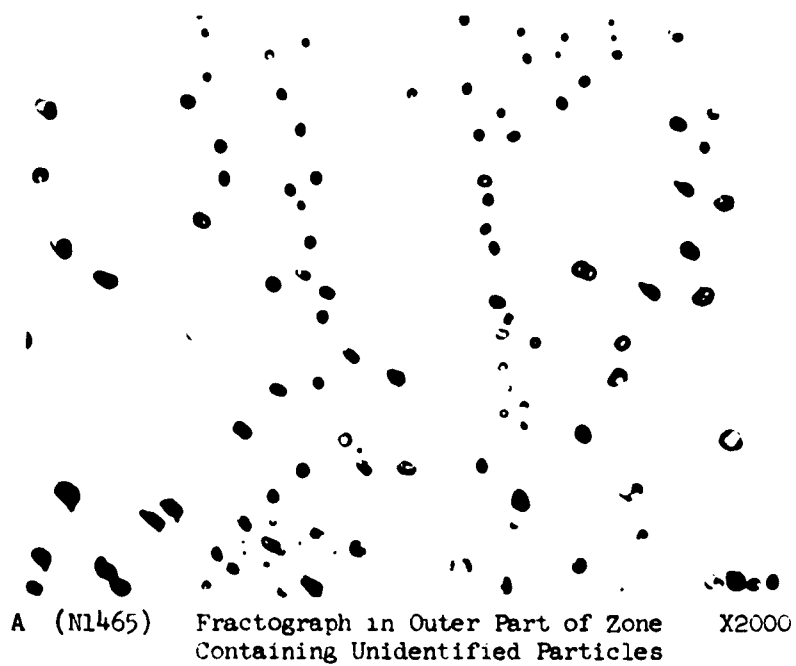


FIGURE 12 - Fractographs of Same Specimen as in Figure 11,
but After Additional Treatment in Vacuum at
3250 F for 66 Hours and 3600 F for 2.5 Hours



A (N1493)

Fractograph

X2000

B (N1490)

Electropolished Only

X2000

FIGURE 13 - Microstructure of Unalloyed Molybdenum After Decarburization Treatment. The treatment consisted of heating in 50 μ Hg oxygen for one hour at 2200 F + one hour at 2800 F, followed by heating in 2 μ Hg vacuum for 16 hours at 3000 F + 20 hours at 3250 F.

A (M1488)

Fractograph

X2000

B (M1491)

Electropolished Only

X2000

FIGURE 14 - Microstructure of Same Specimen as in Figure 13,
but After Additional Treatment in Dry, Palladium-
Diffused Hydrogen at 3050 F for 67.5 Hours at
About 1 mm Hg Pressure

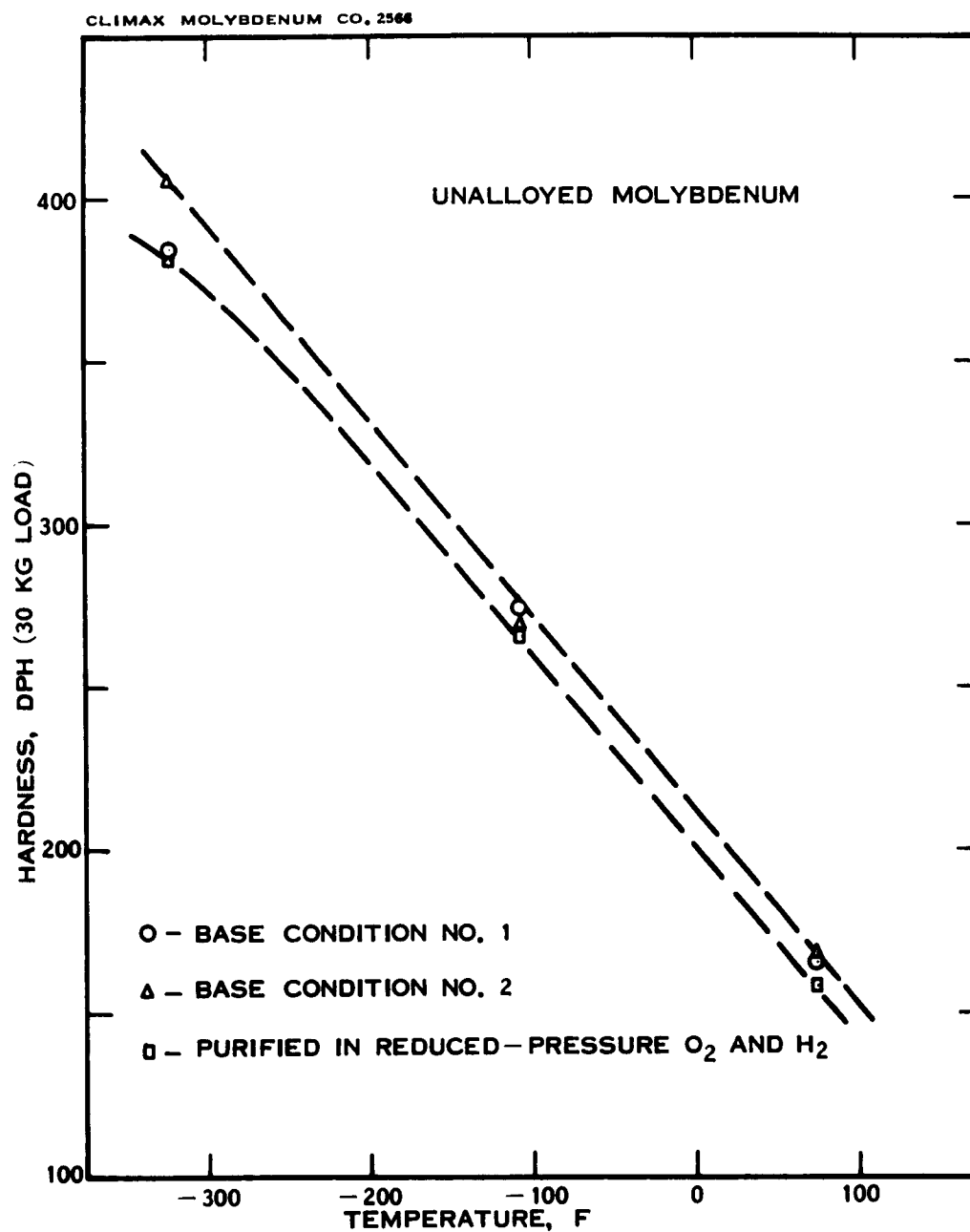


FIGURE 15 - HARDNESS VS TEMPERATURE DATA FOR UNALLOYED MOLYBDENUM BEFORE AND AFTER SOLID-STATE PURIFICATION IN REDUCED-PRESSURE O₂ AND H₂

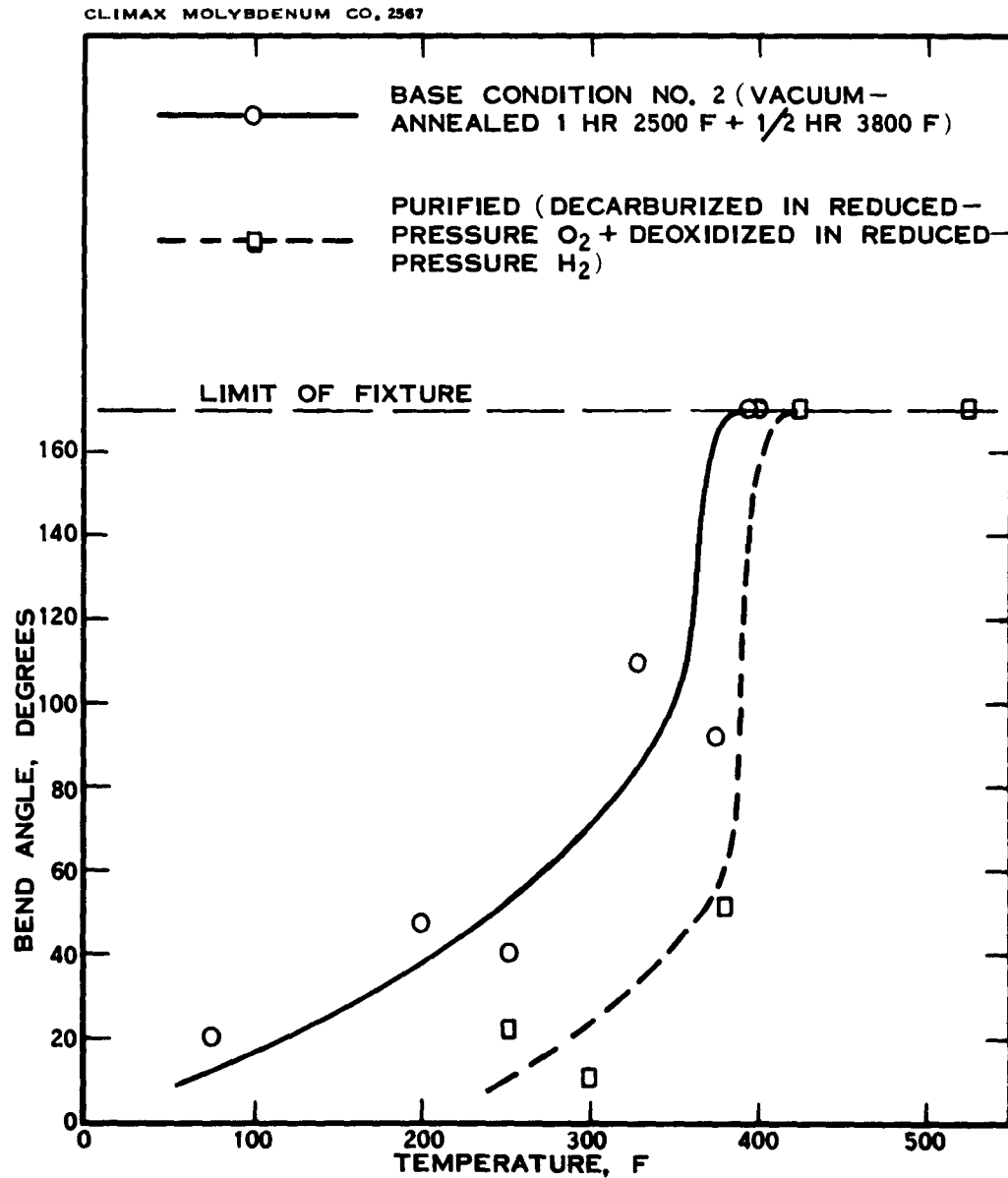


FIGURE 16 - COMPARISON OF BEND TEST RESULTS FOR UNALLOYED MOLYBDENUM BEFORE AND AFTER DUPLEX SOLID-STATE PURIFICATION TREATMENT IN REDUCED-PRESSURE OXYGEN AND DRY, PALLADIUM-DIFFUSED HYDROGEN ATMOSPHERES

APPENDIX

Sample Calculation of Statistical Parameters from Hardness Data*

Material: Unalloyed Molybdenum (Climax Heat 2312-A)

Condition: Purified in Solid State (State 5 in Table 1)

Surface Preparation: Hand polished through 3/0 paper prior to recrystallization.

Type of Hardness Test: Diamond Pyramid Hardness (30 kg load)

Data and Calculations:

<u>H</u>	<u>$\bar{H}-H$</u>	<u>$(\bar{H}-H)^2$</u>	<u>H</u>	<u>$\bar{H}-H$</u>	<u>$(\bar{H}-H)^2$</u>
155	3.5	12.25	159	-0.5	0.25
157	1.5	2.25	161	-2.5	6.25
156	2.5	6.25	160	-1.5	2.25
161	-2.5	6.25	160	-1.5	2.25
157	1.5	2.25	158	0.5	0.25
160	-1.5	2.25	158	0.5	0.25

$$N = 12; \Sigma H = 1902; \bar{H} = \frac{\Sigma H}{N} = 158.50 \text{ DPH.}$$

$$\Sigma(\bar{H}-H)^2 = 43.00.$$

$$\text{Unbiased Estimate of Variance} = S_H^2 = \frac{\Sigma(\bar{H}-H)^2}{N-1} \text{ (for single impressions).}$$

$$S_H^2 = \frac{43.00}{11} = 3.91; S_H = 1.977.$$

$$\text{For means based on } M \text{ impressions, } S_{\bar{H}} = \frac{S_H}{\sqrt{M}}.$$

$$\text{For means based on 12 impressions, } S_{\bar{H}} = \frac{1.977}{\sqrt{12}} = 0.572.$$

95% Confidence range for means from three impressions:

$$\bar{H} \pm (t_{.025}) (S_{\bar{H}}) = 158.50 \pm (2.201) (0.572) = 158.50 \pm 1.26 \text{ DPH.}$$

* Reference 5 may be consulted if more information about the parameters is desired.